CRUISE REPORT ECO2-7
(Panarea Island, Italy)
May 21-31, 2013

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Summary

1 INTRODUCTION

Carbon capture and storage (CCS) is expected to provide an important, short-term approach for mitigating potential global climate change due to anthropogenic emissions of carbon dioxide (CO_2). This technology involves the capture of CO_2 emitted from large point sources and its injection into deep geological reservoirs, such as depleted hydrocarbon reservoirs and deep saline aquifers, both on land and off-shore. Offshore reservoirs are particularly favourable due to potentially high storage capacities, the extra barrier provided by the overlying water, and the physical separation between injection sites and populated centres. The 14-year old Sleipner project, in the North Sea, is the world's first and largest pilot-scale CCS project; here about 1 million tonnes of CO_2 are injected per year into a deep saline aquifer

Despite the safe track record at Sleipner, several concerns exist amongst various stakeholders regarding the long term safety of sub-seabed CO_2 storage, including the potential for leakage of CO_2 and associated gases/compounds into the water column (with potential impacts on the marine ecosystem) and possible migration to the atmosphere. In addition, due to greater logistical problems, marine sites have been studied much less than terrestrial systems regarding site characterisation, monitoring, leakage detection and quantification, ecosystem impact, and human health and safety.

Although laboratory experiments and modelling can be performed, for a more complete (and realistic) understanding of a possible seabed leak of CO_2, it is preferable to study natural, analogous systems. This is particularly important because CO_2 leakage presents some unique challenges. First, it is highly soluble and thus CO_2 bubbles will dissolve extremely rapidly; this makes bubble detection more challenging using hydroacoustic techniques. Second, dissolved CO_2 increases the density of seawater, and thus high CO_2 concentration seepage will likely remain closer to the seafloor.

Because of these complications, the Università di Roma "La Sapienza" and OGS first proposed the inclusion (within the ECO2 project) of the natural, shallow analogue site near the island of Panarea (Aeolian Islands, Italy; Fig. 1), where natural, thermo-magmatic CO_2 is leaking at substantial rates from the seafloor at water depths ranging from 5 to 30 m. This CO_2 is released most strongly in the area surrounding two of islets located 3 km to the east of Panarea (Lisca Bianca and Bottaro). This natural CO_2-release field (c. 3 km^2) has been active for centuries, with gas emanating from a series of NW-SE and NE-SW trending fractures (Esposito et al., 2006). In the early 1980's researchers began to conduct gas geochemistry surveys of the area (Caliro et al., 2004), showing that the system was relatively stable in both gas chemistry (e.g. 98% CO_2, 1.7% H_2S plus other trace gases) and flux rates (7-9 x 10^6 l/d). On November 2 and 3, 2002, a gas outburst event increased the total gas flow rate by about 2 orders of magnitude (4 x 10^8 l/d) (Caliro et al., 2004), with large volumes of gas reaching the water surface. Flux rates began to decrease towards pre-outburst conditions about 3 months after the event. Most release points are gas only, although various points also release water of different origin, ranging from geothermal to seawater end-members that are mixed to variable degrees (Tassi et al., 2009).

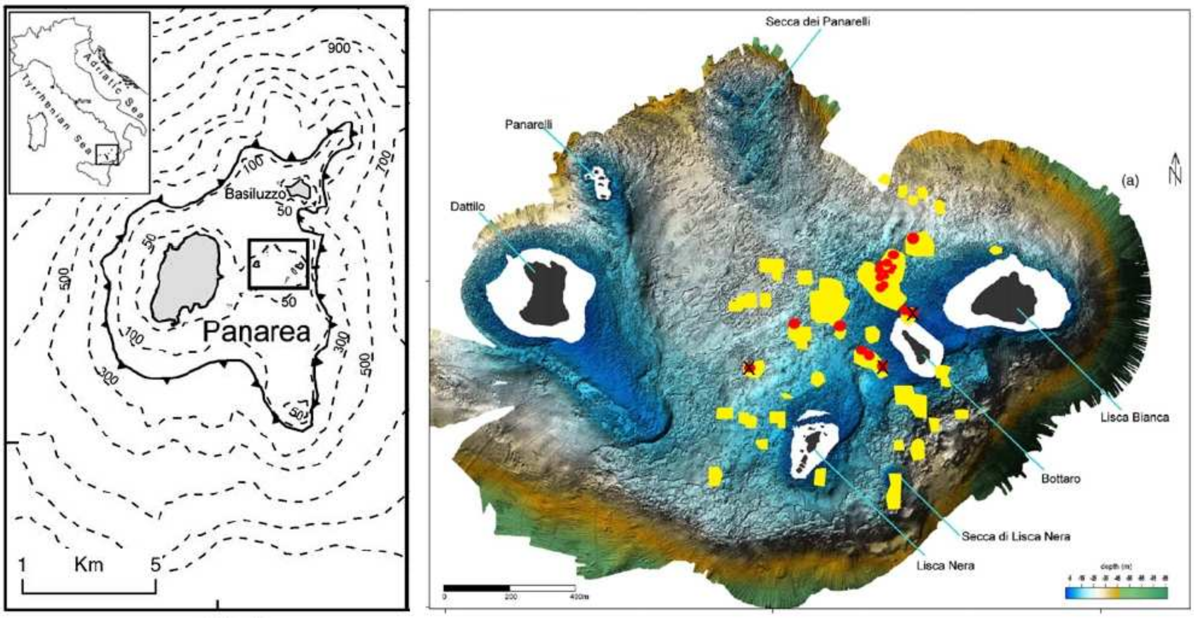


Figure 1 Map (left) showing Panarea Island and associated islets to the east (boxed area). Bathymetric map (right) showing the location of the gas leaks in December 2002 (yellow) soon after the outburst, the three strongest gas release points during the outburst (x), and the gas leak locations one year later (red circles). Modified after Esposito et al. (2006).

Based on the range of depths and relatively high and persistent gas flow rates, the occurrence of both gas only and gas-water seepage, and its close proximity to shore (Fig. 1b), Panarea represents an exceptional location to study natural processes and impacts related to shallow seabed CO_2 leakage.

The present report details work conducted at the Panarea site by UniRoma1 and OGS within the ECO2 project from May 21 – 31, 2013. Due to very rough weather during this period, only a portion of the planned work could be completed.

2 OBJECTIVES

Research conducted at the Panarea site by UniRoma1 and OGS within the ECO2 project is within the framework of three separate work packages: WP2, WP3, and WP4. The following lists the original goals of this cruise.

WP2 ("Fluid and Gas Fluxes across the Seabed at Storage Sites and Natural CO_2 Seeps"):

- Conduct gas bubble flux measurements using the accumulation chamber method. Work focused on three profiles across different leakage areas (with sampling at regular intervals) to better estimate total flux rates, and on periodic sampling of three fixed points to examine temporal variability.
- Perform benthic chamber measurements at sites where there is a flux of deep water which only contains dissolved CO_2 but no gas bubbles. The chamber was sampled for major and trace elements and carbonate system parameters. A pCO_2 probe was deployed within the chamber for continuous monitoring, and shallow piezometers were installed to different depths in an effort to use vertical profile concentration trends as a second flux estimate technique to compare results with the benthic chamber data.

WP3 ("Fate of CO_2 and other Gases emitted at the Seabed"):

- Study gas exchange processes between an ascending CO_2 bubble and the surrounding water column through the use of video filming, gas bubble chemistry analyses, and water column chemistry analyses.
- Deployment of a total of 20 pCO_2 probes (developed by the University of Rome) along a 2D transect perpendicular to the main current direction and about 3 m away from a main leakage area. Measurements every 10 minutes by all probes will yield temporal changes in dissolved CO_2 concentrations and distributions, for better understanding fate of CO_2 in the water column.

WP4 ("Impact of Leakage on Benthic Organisms and the Marine Ecosystems"):

- Water sampling to examine the effect of increasing pCO_2 on the planktonic ecosystem.

- Sediment sampling to determine impacts on benthic fauna (microphytobenthos and meiobenthos).
- Primary and secondary benthic production experiments in areas of fluid leakage.

Rough seas during the present cruise stopped the field samplings and experiments on different occasions, causing a strong delay in the original work schedule. This compromised the activities planned for achieving the goals described above, and thus not all work could be completed. Nevertheless a supplementary field campaign has now been scheduled for October 2013 to complete all planned research.

3 SUMMARY OF WORK

3.1 Participants

Family name	Name	Background	Institute
Beaubien	Stan	Geochemist	UniRoma1
De Vittor	Cinzia	Biologist	OGS
Comici	Cinzia	Geologist	OGS
Franzo	Annalisa	Biologist	OGS

3.2 Narrative

Tuesday, May 21st

- 18:00 UTC: Departure from Naples with the ferry bound for the Aeolian Islands

Wednesday, May 22nd

- 06:00 UTC: Arrival on Panarea Island
- 07:00 UTC: Unpacking and set-up of the on-land laboratory

Thursday, May 23rd

- Rough seas
- Briefing with the diving- and boat- support staff from 'Amphibia' diving center, Panarea

Friday, May 24th

- Rough seas

Saturday, May 25th

- 8:00 UTC: deployment of all pCO_2 probes in a single block for system testing and inter-calibration.
- 8:30 UTC: The water column profile was measured at Basiluzzo Island (B1 and B2) by means of a CTD (Seabird 19 Plus) and the sampling of water was performed at discrete depths (0.2m, 7 m and 13 m) using Niskin bottles.
- 13:00 UTC: Laboratory analysis
- 16:50 UTC: gas bubble accumulation chamber measurements
- 17:50 UTC: recovery of block of pCO_2 probes
- Rough seas

Sunday, May 26th

- 9:50 UTC: Sediment sampling off Basiluzzo Island (St. B1)
- 9:50 UTC: Primary and secondary benthic productions experiments
- 10:15 UTC: Water column profile by means of a CTD

Monday, May 27th

- 9:00 UTC: Sediment sampling off Basiluzzo Island (St. B3 and St. B2)
- 9:00 UTC: Primary and secondary benthic productions experiments

- 9:00 UTC: deployment of a pCO_2 probe at sediment interface as support for productivity experiments.
- 12:30 UTC: Water column profile by means of a CTD
- 14:00 UTC: deployment of 20 pCO_2 probes along a 2D transect down-current from a major CO_2 leakage area (i.e. the Crater).

Tuesday, May 28th
- Rough seas

Wednesday, May 29th
- 11:00 UTC: Benthic chamber measurements off Panarea Island
- 13:30 UTC: installation and sampling of shallow sediment peizometers
- 13:40 UTC: Sediment sampling off Panarea Island
- 14:40 UTC: Water column profile by means of a CTD
- 15:00 UTC: Laboratory analyses

Thursday, May 30th
- 8:00 UTC: Water column profile by means of a CTD at Crater station off Bottaro Island
- 8:30 UTC: recovery of pCO_2 probe transect
- 9:30 UTC: rough seas
- 9:30 UTC: Laboratory analyses, cleaning and packing of equipment
- 18:00 UTC: Embark on ferry to Naples

Friday, May 31st
- 06:00 UTC: Arrival at the Port of Naples

4 DESCRIPTION OF WORK

Note that all work was conducted from a 8.5 m long inflatable Zodiac boat.

4.1 Water column sampling (Basiluzzo Island)

Two stations, located just off the eastern tip of Basiluzzo Island and defined during the ECO2-4 and ECO2-6 cruises (June 2012 and October 2012, respectively), were sampled during this field campaign:

- station B1 (38°39.749’ N, 15°07.132’ E), characterized by gas emission
- station B2 (38°39.827’N, 15°07.118’E) without gas emission, referred to as the control site.

The physical characterization of the water column was performed using a CTD (SeaBird 19 plus) equipped with the sensors described in Table 1. These sensors are calibrated on a regular basis in the OGS calibration laboratory.

Table 1. Technical characteristics of the sensors mounted on the CTD probe.

PARAMETER	RANGE	ACCURACY	RESOLUTION
Temperature (°C)	-5 to 35	0.005	0.0001
Conductivity (S/m)	0 to 9	0.0005	0.00007 S/m (resolves 0.4 ppm in salinity)
Pressure (strain gauge)	0 to 100	0.1% of full scale range	0.002% of full scale range
Fluorescence (Scufa submersible fluorimeter)	4 orders of magnitude		12 bit
pH (SBE18)	0-14 pH	0.1 pH	
Dissolved Oxygen (SBE43)	120% of surface saturation	2% of saturation	

The resultant CTD data, which defines water column stratification and pH distribution, were used to choose the depth of discrete water samples (at three levels) for various chemical and biological analyses, including: dissolved oxygen, pH, alkalinity, dissolved inorganic nutrients, dissolved organic phosphorous and nitrogen, particulate total carbon, particulate organic carbon, dissolved gasses and H_2S concentration, phytoplankton abundance and diversity, microzooplankton abundance and diversity and prokaryote abundance. The rates of prokaryotic carbon production have also been examined.

All samples were placed in coolers with ice packs on the boat until transfer to the land laboratory on Panarea Island. Samples for oxygen and pH were immediately analysed, while those for particulate organic and inorganic matter were filtered and filters were frozen until return to the laboratories at OGS. Samples for prokaryotic carbon production and prokaryotic abundance were stored at 4°C until the return at OGS laboratories.

4.2 Sediment sampling (Basiluzzo and Panarea Islands)

Sediment samples were collected for the analyses of abiotic parameters (sediment grain-size, Total Organic Carbon, Biopolymeric Carbon, pigments) and benthic communities (picobenthos, microphytobenthos and meiofauna). A total of five stations were sampled: three near Basiluzzo Island previously identified with our ECO2 colleagues MPI/Hydra (station B1, "Red with Gas" - 38°39.749'N, 15°07.132'E; station B2, "Grey no Gas" - 38°39.827'N, 15°07.118'E; and station B3, "Grey with Gas" - 38°39.82'N, 15°07.137'E), and two just NE of Panarea Island (38°38.536'N, 15°04.714'E) where the sediments are characterized by very different temperatures at a distance of approximately 1 m one from another. This last site is referred to here as "Hot-Cold" (HC) and by partners MPI-Hydra as site "Corpi Morti".


a)

b)

Figure 2. Sampling of sediment by scuba diver (a); extrusion of sediment cores and surface layer subsampling (b)

Virtually undisturbed sediment cores were collected by scuba divers using cut-off plastic syringes (2.7 cm i.d., length 11.4 cm) and then the lowermost side was closed with a plastic cap (Figure 2a). Samples of abiotic parameters, picobenthos and meiofauna were collected in triplicates and immediately stored at –20°C until subsequent processing in the OGS laboratories. For chemical analyses, the sediment cores were partially extruded and only the surface layer (1 cm thick) was collected (Figure 2b). For microphytobenthos the surface sediment layer was collected in triplicates, fixed with 4% formaldehyde/filtered sea water and stored at 4 °C.

4.3 Primary and secondary benthic production (Basiluzzo Island)

During this campaign, functional parameters, i.e. primary and secondary benthic production, were measured at the three sites near Basiluzzo Island (St.s B1, B2 and B3) where the other benthic parameters were collected.

Primary Production (PP) was estimated using the ^{14}C incubation method (Cibic et al., 2008 modified for coarse sediments). Two sediment cores were collected at each site by scuba divers using cut-off plastic syringes (2.7 cm i.d., length 11.4 cm). The surface layer (0.5 cm thick) was extruded and re-suspended in 100 mL of previously filtered (0.2 μm) *in situ* sea water. After inoculation of 500 μL of $NaH^{14}CO_3$ (10 μCi), 9 mL of the slurry was transferred into 9 glass vials divided as follows: 3 replicates to assess the sediment matrix effect, 3 dark replicates and 3 light replicates. Carbon incorporation was immediately stopped in the first 3 vials adding 100 μL of HCl (5N). The other vials were incubated *in situ* for 1 hour. At the end of the incubation period, carbon incorporation was stopped in all vials.

Secondary benthic production (PCP, Prokaryotic C Production) was measured using the ^{3}H-Leucine (Leu) incorporation method (van Duyl and Kop, 1994 as detailed by Manini et al., 2004). As for PP, two sediment cores were collected at each site by scuba divers using cut-off plastic syringes. The surface layer (0.5 cm thick) was extruded and homogenized. Aliquots of 200 μL were subsampled in 5 plastic vials (2 controls and 3 replicates). After the addition of ^{3}H-Leu (6 μCi) to all the subsamples, the radiotracer incorporation in the controls was stopped by adding 80% ethanol (1.7 mL) while the other vials were incubated in the dark and *in situ* for 1 h together with samples of PP. After incubation, 1.7 mL of 80% ethanol was added to the incubated vials. The samples of PP and PCP were stored at 4°C until the subsequent processing at the OGS laboratories.

4.4 Dissolved constituents flux (Panarea Island)

The benthic chamber experiment was conducted at the hot counterpart of the Hot-Cold (Corpi Morti) site described above (38°38.536'N, 15°04.714'E), where small areas (c. 1-2m in diameter) of hot sand are surrounded by normal temperature sediments. The benthic chamber was used to measure the flux of dissolved CO_2, heat, various carbonate system parameters, and major and trace elements from the sediments to the overlying seawater. Measurements were made on the assumption that the hot sediments are an indication of deep, hydrothermal waters that are migrating to the surface via preferential pathways.

The experiment was conducted as follows. First a pCO_2 probe was placed on the hot measurement point and left for 10 minutes to equilibrate with the surrounding conditions. After this period, water samples were collected from right beside the probe, just above the sediments, and then the benthic chamber was placed over probe (Figure 3a). Samples were then collected from the chamber 3 times (once every 10 minutes) Collected water samples will be analysed for dissolved inorganic carbon (DIC), dissolved oxygen, hydrosulfide, pH, dissolves gasses, anions and cations.

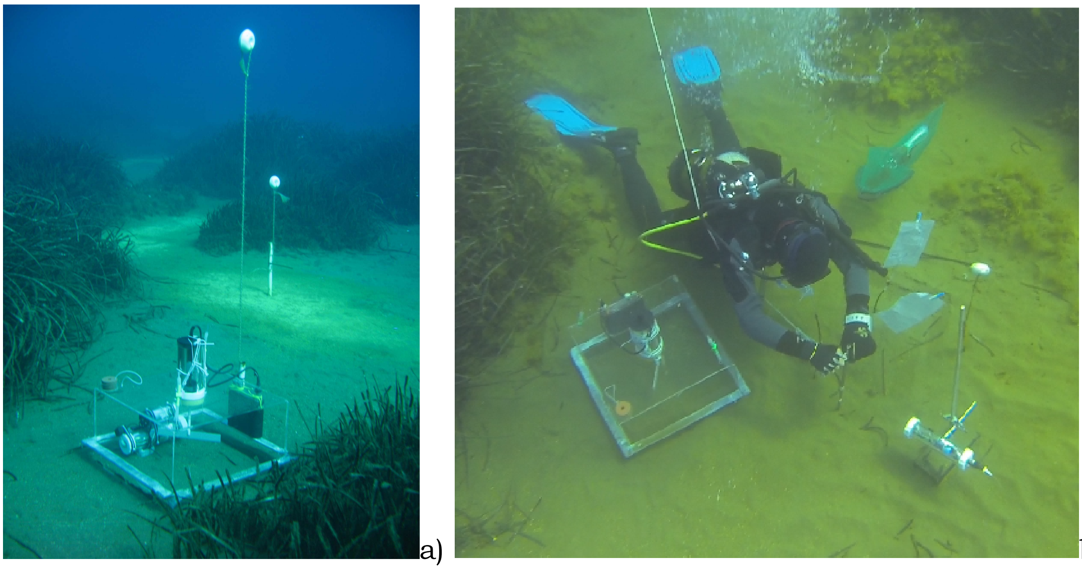
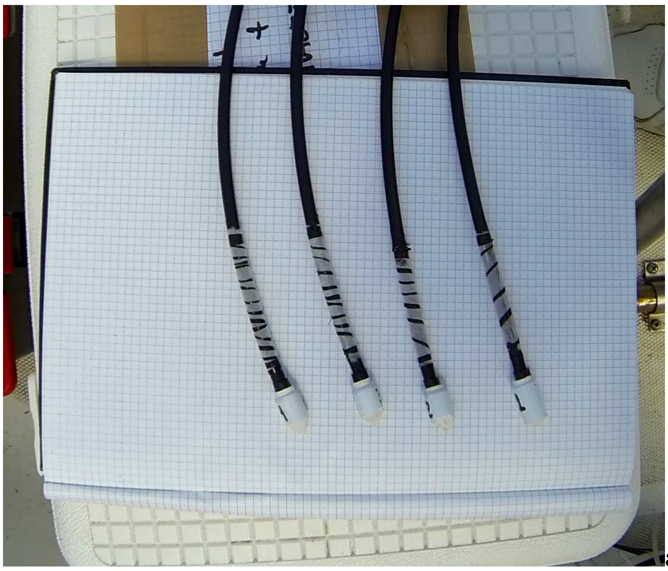

a) b)

Figure 3. Benthic chamber deployed at the cold sand site at the Corpi Morti, with the pCO_2 sensor deployed within the chamber (a). Installation of the shallow sediment "piezometers" in the hot sand site, with sampling bags attached to the already installed tubes (to the right of the diver) (b).

In an effort to collect supplementary data to support the interpretation of the benthic chamber results, shallow sediment piezometers were installed at different depths at the hot site within the footprint of the benthic chamber after its measurement was complete (Figure 3b). The resulting vertical distribution of dissolved constituents will also be used to calculate flux rates.

Small diameter (6mm) plastic tubes were modified for this purpose, with a plastic drive point mounted on the bottom end just below a 5 cm long perforated interval that was covered with permeable material (Figure 4a). For installation, each piezometer was inserted into a slightly wider diameter steel tube (Figure 4b) which was used to hand-push the piezometer tip to the desired depth (Figure 3b). The four piezometers were deployed to 10, 20, 30, and 40 cm depths. Initially plastic medical bags were attached to the tubes in the hope that the pressure gradient would fill them naturally (avoiding any depressurization), however only one bag filled slightly and thus all tubes were sampled using plastic syringes and the collected water was transferred into sample bottles in the boat. Because of the small volume of water obtained from each piezometer, samples were collected for the analysis of pCO_2, pH, and DIC only.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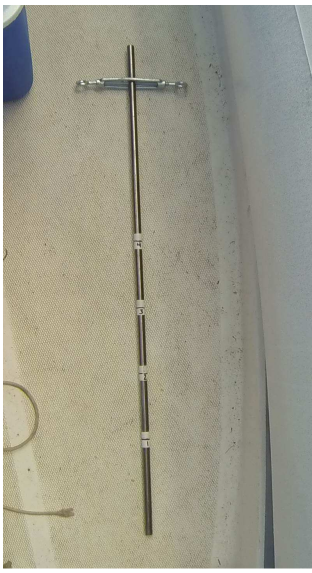

b)

Figure 4. Shallow sediment piezometers (a) and the rigid tube used to install them (b).

4.5 pCO_2 probe transect (Bottaro Island)

A total of 20 pCO_2 probes, developed by the University of Rome La Sapienza, were built, tested, and calibrated in the laboratory prior to the present cruise, with the goal of deploying all units along a 2D transect to study temporal and spatial variations of dissolved CO_2.

Initial work involved deployment of all units together as a single block within the studied leakage area (i.e. the "crater") for a single day (Figure 5) to allow for testing of the individual units (e.g. water tightness) and to compare measured concentrations in the study environment to ensure an accurate inter-calibration of the probes. This phase was crucial to allow for small corrections in measured values during the experiment, especially at the low concentration range, to ensure an accurate representation of the system.

The block of probes were deployed for a period of about 6 hours, with a measurement frequency of once every 10 minutes. As shown in Figure 5, the units were initially deployed with the measurement membranes facing upwards (so all probes would be measuring the same water depth; unfortunately, due to very strong currents, the block fell on its side, meaning that the bottom row of probes were almost in contact with the sediments, whereas the top row was about 30 cm above the sediments. The units were recovered at the end of the same day they were deployed, the results downloaded, and the probes were readied for the actual experiment (which started 2 days later).

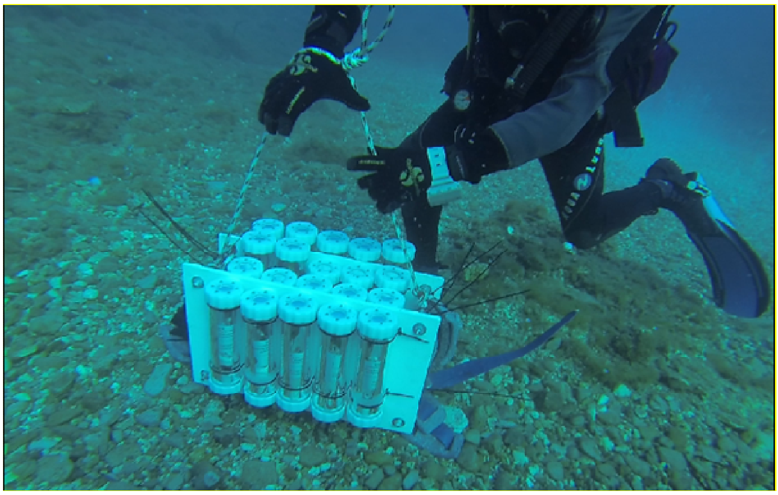
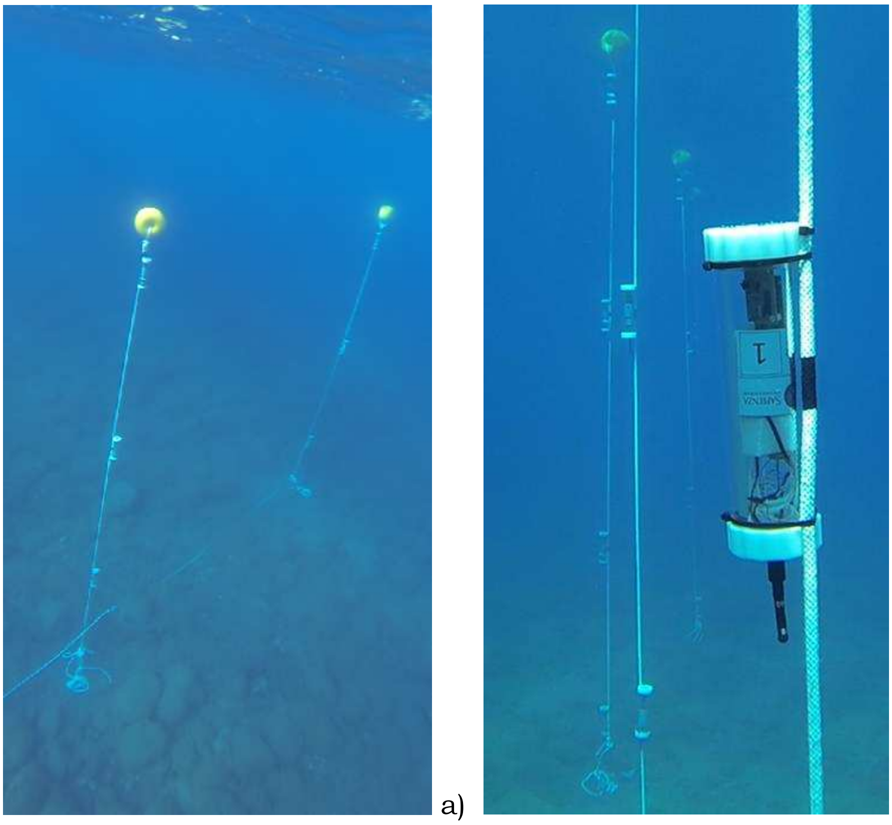


Figure 5. Photograph showing the deployment of all probes together for initial testing and inter-calibration.



a) b)

Figure 6. Photographs showing the pCO_2 probe transect after deployment. Note in (b) that the probe membranes were placed facing up to prevent gas bubbles from coming in direct contact.

The 20 probes were mounted on 5 cords held vertically using c. 20L anti-collapse buoys (Figure 6) and held in place using at least 20 kg of ballast each. The points of ballast deployment were located about 5 m from each other and about 3 m from the edge of the crater, along a line perpendicular to the main current direction and to the long axis of the crater itself (Figure 7a). The probes were fixed to the ropes at regular intervals, with the shallowest row at about 2m below the water surface and about 2m between each row (except for the last row) (Figure 7b). As the bathymetry slopes slightly away from Bottaro Island, the last row of probes were all placed at a fixed distance of about 30cm above the sediments

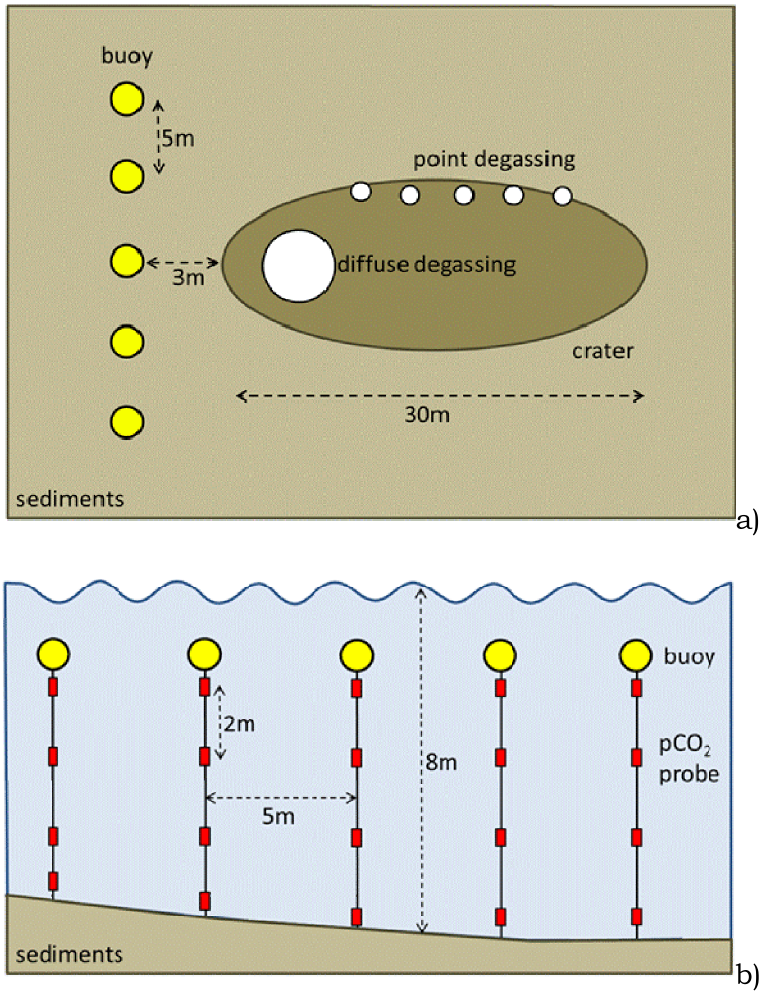


Figure 7. Schematic diagrams showing the spatial distribution of pCO_2 probe transect, both in map view (a) and in cross-section (b).

The deployed probes were programmed to measure once every 10 minutes for pCO_2 and for water temperature. In addition, two probes (the top and the bottom probes in the left-most column in Figure 7) were equipped with pressure sensors to measure tidal fluctuations and give a very rough estimate of wave activity.

After a deployment time of about 3 days, the probes were recovered and the data downloaded. All probes functioned properly for the entire experimental period, and initial data processing shows very promising results.

4.6 Gas bubble flux measurements (Bottaro Island)

Two types of gas bubble flux measurements were planned for this campaign, one that examined temporal variations and another that looked at spatial variations. Although this work was started, only very limited sampling could be conducted due to rough seas. This work will be continued during the summer in agreement with the technical support divers at Amphibia.

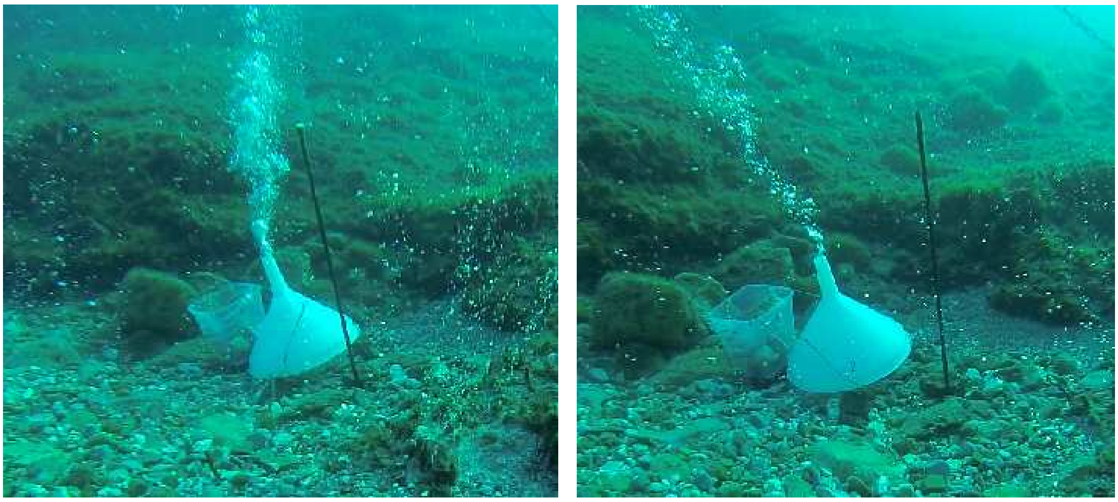


Figure 8. Screen-capture photographs of a video of one fixed gas-bubble-flux measurement point, with the two frames taken about 3 to 4 seconds apart. Note the strong difference in flux rate, linked to the large waves occurring during that day (i.e. height of the water column, and thus confining pressure).

Temporal variations were studied by fixing three large funnels at points representative of the three flux areas mapped in the previous campaign (Beaubien et al., 2012) (Figure 8). The original plan was to sample these three points repeatedly over the arc of a single day, in correspondence with tidal variations, to monitor total flux rates. It is interesting to note that in addition to this hypothetical low frequency variation, video footage of one of the strong point leakage sites shows how flux rate can also vary at higher frequency rates due to the height of the water column and associated confining pressure, as shown in the two video frames taken about 3 seconds apart (Figure 8). Unfortunately, due to rough seas, it was only possible to deploy the funnels and make the initial measurements before this work had to be halted.

Spatial variations were to be addressed by conducting three horizontal profiles across each of the three mapped zones, with the measurement of bubble flux at regular intervals along each line (Figure 9). Sample spacing ranged from 1 to 3 m depending on the total length of the profile, for a total of about 10 measurements per zone. This work was to determine a more accurate average value (i.e. one that integrates wide range of flux rates observed within each zone) for the calculation of the total flux rate from the crater area. Again this work was started, with the deployment of the line across the strong diffuse zone (Figure 9) but was halted due to bad weather.

Figure 9. Photograph showing one of three profiles traced across the different flux zones in the crater area (this is across the strong diffuse zone). Accumulation chamber measurements were made once every 1 to 2 m to obtain a more accurate total flux estimate for each area.

4.7 Gas bubble video experiments (Bottaro Island)

This planned work had to be cancelled due to rough seas.

5 SUMMARY

Work was performed at the Panarea natural laboratory by personnel from the Università di Roma La Sapienza and OGS during the period May 21 to 31, 2013 within the framework of Work Packages 2, 3, and 4 for the EC-funded research project ECO2. As for the previous field campaigns, research was divided into three main themes focussing on: i) chemical and biological processes in the sediments and along the water column; ii) the flux of gas bubbles and deep-origin brines from the sediments to the water column; and iii) the fate of gas bubbles within the water column.

Water sampling was conducted successfully at the two stations close to Basiluzzo Island (B1 and B2) continuing the previous works done during the field campaigns of 2012.

Sedimentary work was concentrated on two areas, one off the east coast of Basiluzzo Island and another just to the NE of Panarea Island itself (Corpi Morti). This work was conducted at the same sites as the previous campaign in October 2012, with an expanded list of analysed parameters. The only difference is that the primary and secondary production experiments have been performed near Basiluzzo Island instead of Corpi Morti. All planned measurements were successfully performed for this task.

The flux of dissolved constituents was again successfully repeated, with benthic chamber deployments near Panarea Island at a site where CO_2-rich, warm water is being discharged from the sediments into the overlying water column. In addition, a new type of measurement was conducted at this site, with the installation and sampling of shallow sediment piezometers at different depths below the water-sediment interface. The resultant vertical distribution of the measured carbonate parameters will be used to calculate flux rates for comparison with the benthic chamber results.

A completely new, and highly unique, experiment was conducted with the deployment of 20 autonomous pCO_2 probes deployed along a 2D transect in the water column, located about 3m away from the large gas leakage area within the crater and oriented perpendicular to the main current direction. These probes were programmed to measure dissolved CO_2 and temperature (as well as pressure in two probes) once every 10 minutes for the entire deployment time of about 3 days. Data processing is underway to create video animation which shows the concentration distribution of dissolved CO_2 across this transect and how it changes over time.

Bubble flux measurements, focussing on both temporal and spatial variability in the “crater” site near Bottaro Island were started, however very few measurements were conducted before work had to be stopped due to bad weather. An agreement has been made with the technical divers at Amphibia to complete this work during the summer.

Planned work on gas bubble video experiments and the sampling along a water column transect near Bottaro Island could not be performed due to bad weather.

Although several days of bad weather limited, or completely stopped, the work planned for this campaign, these items and others will be addressed in the newly added cruise planned for October 2013.

6 ACKNOWLEDGEMENTS

We thank Andrea Fogliuzzi and his assistant Simona from the Amphibia Diving Center (Panarea, Italy) for their invaluable help in conducting these experiments.

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